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On-Line XRF Analysis of Phosphate Materials at Various Stages of Processing

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Abstract

Potential applicability of X-ray fluorescence conveyor analyzer CON-X03 was demonstrated for the quantitative on-line measurement of P, S, Cl, K and Ca in several types of ground phosphate rock, phosphate fertilizers and intermediates at various stages of phosphate processing. In addition to the physical components required to perform on-line XRF measurements, the analyzer is equipped with special evacuated mini-chamber. Assessment of calibration quality for P, S, Cl, K and Ca was demonstrated on the basis of control samples and synthetic mixtures. The dynamic simulation of on-line measurements of ground N-P-K fertilizers continuous flow indicated a statistically acceptable correlation with laboratory chemical analyses (relative standard deviation for P is better than 2.0%, for S and K – better than 10% relative). Application of on-line conveyor XRF analyzer to industrial processing generates real-time feedback of elemental composition and quality of phosphates moving on the conveyor thus enables to automate control of the production processes.

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Keywords: on-line XRF analysis, phosphorus fertilizers, traces of chlorine and uranium;

1. Introduction

Phosphates in the form of fertilizers play an important role in agriculture, since phosphorus is a critical component of the soil, ensuring both the development of plants and being essential dietary component. According to various sources, about 90-95% of the world's supply of phosphate ore is consumed for the production of fertilizers. In addition, phosphates are used in different areas of the chemical industry.

There are five main types of phosphate deposits, depending on the origin of occurrence: marine sediments (75%), volcanic, metamorphic, and resulting from soil erosion (15-20%), as well as biogenic ones. Note that sedimentary rocks are generally characterized with the lower phosphate content.

Obviously that economically viable is to extract phosphates from fields with high natural content of phosphorus. However, in general, the extracted ore is of low grade, and for industrial applications it should be concentrated before processing. On top of this, due to the increasing consumption of phosphate ores for the production of mineral fertilizers, mining and processing of the lower grade bedding are becoming more and more often.

Several methods of beneficiation are used in order to upgrade quality of the ore. Selection of the combination of techniques depends both on the type of the field, and on the form of gangue material. The main ways of phosphate ores upgrading are: size reduction of ore lumps and screening; abrasive cleaning and classification; electrostatic separation; magnetic separation; chemical dissolution of carbonates and flotation. Note that almost 60% of the phosphate product in the world is manufactured by

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means of flotation [1]. The final goal of phosphate rock processing is the production of phosphoric acid that is mostly consumed for fertilizers manufacturing and agro-food industry.

On-line analysis and automation of processes are powerful tools to optimize the efficiency of technology. Applicability of online analyzers for measurements of material flows has been already proven for the various stages of mineral processing: the incoming express quality control of raw materials, primary beneficiation of ore material (sorting and rejection), grinding and flotation processes, hydro-and pyrometallurgical ones and others [2]. All these require the use of analytical methods with a wide range of possibilities [3], and the method of energy dispersive X-ray fluorescence (EDXRF) is one of them [4]. Lower sensitivity to light elements, namely, Mg, Al, Si, P and S (i.e. components of phosphate materials) considers as a serious disadvantage of XRF. The reason is in strong absorption of X-ray photons of light elements both by material itself and by air. Advantageous output to measure low atomic number elements is a very compact measurement geometry which minimizes the X-ray absorption by air.

CON-X03M is a modified version of the on-line XRF analyzer [5], which uses a close geometry of measuring unit and partial evacuation of air from the measuring space. It was developed and produced specially for measurements of low atomic number elements (Al, Si, P, S and K). The combination of close geometry and partial air evacuation essentially improves sensitivity to light elements. In view of all above, we have focused our laboratory studies on the evaluation of the applicability of CON-X03M analyzer for analysis of phosphorus and associated elements in several types of phosphate fertilizers where the range of phosphorus content is 1 – 25% mass. Besides that the results of laboratory study of analyzer potential applicability to measure ppm contents of chlorine in ground wet phosphate ore and traces of uranium in phosphate rock and products are also described.

Nomenclature

ppm unit of concentration, *parts per million*

2. Ternary fertilizers N-P-K

Ternary fertilizers N-P-K (nitrogen-phosphorus-potassium) were studied to estimate the feasibility of on-line XRF analyser to measure the contents of phosphorus, sulfur, potassium and calcium on product conveyors. Standard samples with similar matrix were not available in our application laboratory. That is why ground samples of granulated fertilizers containing 10 - 22 % mass P_2O_5, 7 - 15% mass SO_3, 0 - 17% mass K_2O and 2 - 5% mass CaO were used as calibration samples. Set of the samples and analytical data were provided by the Customer. In order to reduce the local inhomogeneity samples of granulated fertilizers were ground in laboratory mill to a particle size <0.2 mm. Calibration curves were measured with stationary standard samples.

Sample excitation and measurement conditions are as follows: X-ray tube anode material: Ag; X-ray tube voltage and current: 8.0 kV and 350 μA; measurement time: 300s**;** distance between the sample and analyzer bottom: 2 mm; medium inside XRF measuring unit: vacuum ~ 0.3 Torr; ambient temperature.

Fig.1 demonstrates the spectra of ground samples of NPK fertilizers with different content of the main components. P, S, Cl and K XRF lines increase in proportion to their concentrations. From these spectra it is clear that quantitative determination of P, S, Cl, K, and likely Ca is possible at 5-minute measurements.

Using available calibration samples of the ground NPK fertilizers the analyzer was calibrated for P, S, K and Ca measurements. Taking into account P, S, Cl, K and Ca spectral lines intensities and their concentrations in calibration samples empirical calibrations were plotted as a function of line intensity vs. concentration of the component. As examples, calibration curves for P, S, K and Ca are shown in the Fig.2.

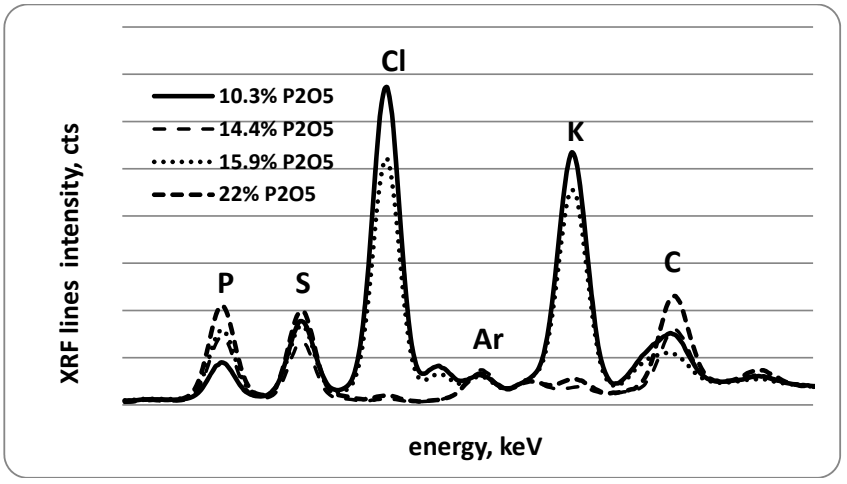

Fig.1. Spectra of ground N-P-K fertilizers (from P to Ca lines). Chemical elements giving rise to the spectral lines are indicated. The Ar line is arising in the air.

These plots demonstrate P, S, K and Ca lines intensity as a linear function of elements concentration. The best fit-line for all points is shown in black together with square of correlation coefficient R^2.

Chemical composition of 4 blind samples provided by the Customer was determined. Results of these measurements were used for cross-check in order to compare measured P2O5 and other component concentrations with Customer reference data and estimate accuracy of analyzer in-house calibrations. Comparison of measured vs. reference data for P and K in blind samples is present in Table 1. Each measured value is an average of 10 measurements (n=2, m=5). Calibration performance was estimated in terms of RMSD (root mean square deviation) the values of which were calculated from differences between measured and reference results.

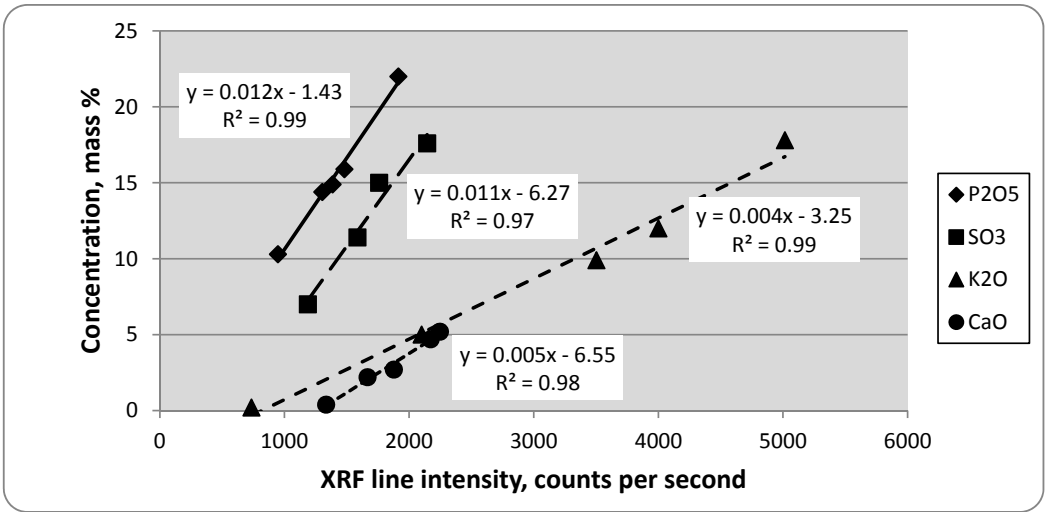

Fig.2. Calibration curves for P, S, K and Ca: measurements were done for ground samples of NPK fertilizers.

Values of RMSD (see Table 1) show that analyzer can measure concentrations of P_2O_5 and K_2O in NPK products with accuracy of 1.5 % relative for P and 7.5 % relative for K. Sulphur results (not indicated here) show correlation with reference values within 8.5 % relative.

Table 1. Measured vs. reference P_2O_5 and K_2O concentrations in the blind N-P-K samples

Sample No	P_2O_5 meas, mass %	P_2O_5 ref, mass %	difference, mass %	K_2O meas, mass %	K_2O ref, mass %	difference, mass %
1	15.98	16.1	0.12	15.9	14.7	-1.2
2	0	0	0	0.1	0	-0.1
3	6.29	6.4	0.11	23.5	23.7	0.2
4	4.98	4.9	-0.08	6.1	5.2	-0.9
average per range, mass %	n/a	6.85	n/a	n/a	10.9	n/a
RMSD, mass%	n/a	n/a	0.11	n/a	n/a	0.82
relative RMSD, rel %	n/a	n/a	1.5	n/a	n/a	7.5

P_2O_5 meas = P_2O_5 measured concentration; K_2O meas = K_2O measured concentration.

Then dynamic simulation of on-line P_2O_5 measurements with CON-X03M analyzer was performed at our XRF laboratory. For this we used ground NPK fertilizers of different composition and laboratory set-up shown on Fig. 3 to ensure continuous flow of ground material along the window of analyzer measuring unit. Results of the tests are shown on the screen-shot of the concentration trend (Fig. 3).

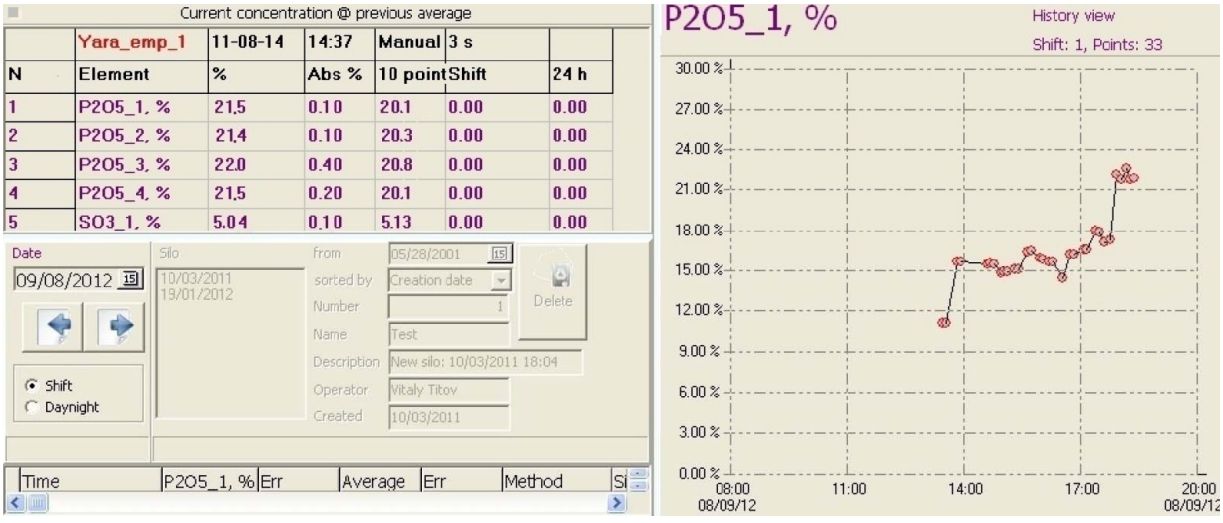

Figure 3. Dynamic simulation of P_2O_5 measurements

Each level of P_2O_5 concentration on the trend corresponds to the materials of different composition. One can clearly see that analyzer discriminates confidently between P_2O_5 content levels.

3. Binary fertilizers N-P and animal feed supplements

Monoammonium phosphate (MAP) and diammonium phosphate (DAP) relate to the group of binary fertilizers. Nominally these products contain two fertilizing elements, P and N. Another group of phosphate fertilizers that we studied was animal feed supplements, namely, monocalcium phosphate (MCP) and dicalcium phosphate ((DCP). Samples of MAP, DAP as well as MCP and DCP were supplied by the Customer. Measurements of their spectra were carried out with the help of CON-X03M analyzer at the same conditions as indicated above (see part 2).

It is clear from visual inspection of these spectra (Fig.4) that qualitative chemical composition of the MAP and DAP samples

is similar, but obviously MAP sample contains higher P and lower S and Ca concentrations compared to DAP sample. P line is prevailing in the spectra of the both products. Because of low atomic number nitrogen line is not seen in the XRF spectra under the conditions of measurement. Potassium line here is poor, i.e. K is available at low concentrations unlike spectra of NPK fertilizers.

MCP and DCP spectra are compared on Fig.5 and 6. Qualitative chemical composition of all samples considered on these figures is similar, but obviously MCP and DCP samples contain higher P and lower Ca concentrations compared to rock samples. P and Ca lines are prevailing in the spectra of all samples.

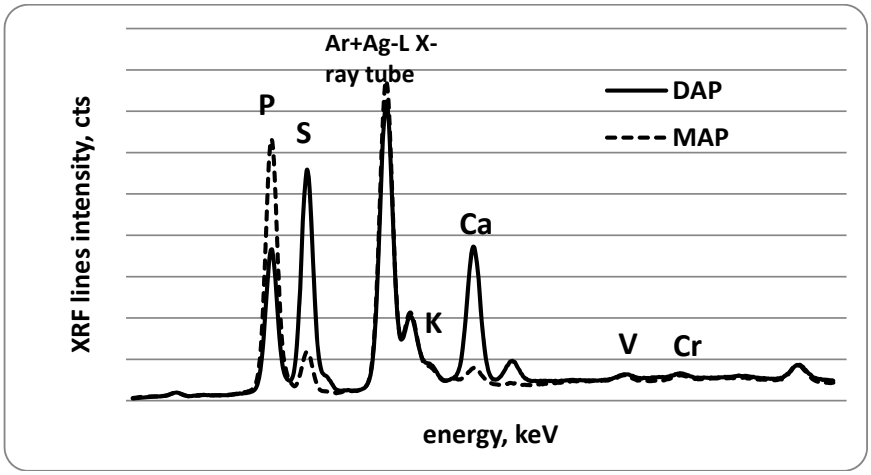

Fig.4. Overview of the spectra of the DAP and MAP samples. Some of the chemical elements giving rise to the spectral lines are indicated. The Ar line is arising in the air; Ag lines have an instrumental origin (X-ray tube anode material)

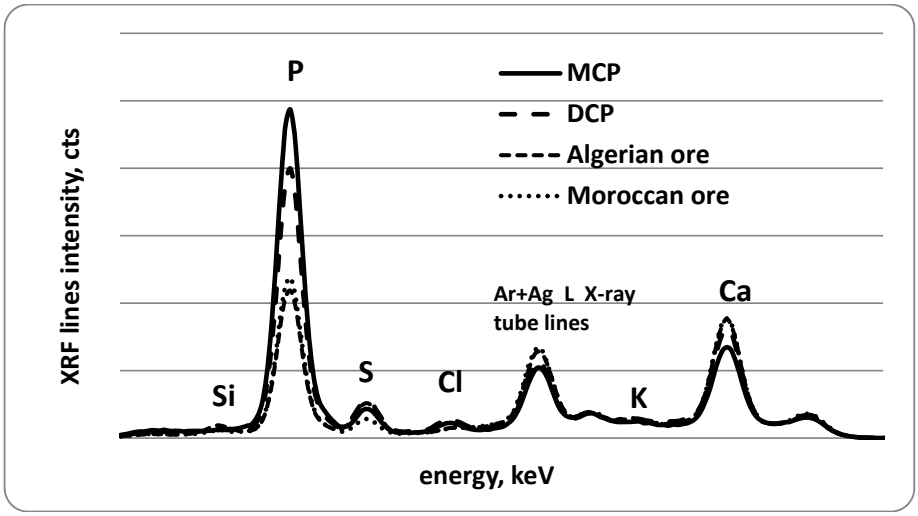

Fig.5. Overview of the spectra of MCP, DCP, Algerian and Moroccan phosphate rocks. The Ar line is arising in the air; the Ag lines have an instrumental origin.

MCP and DCP samples contain very small amounts of Si and more light elements, but rock samples include more high and due to this measurable Si concentrations (see Fig.5). According to the analysis report issued by SGS (Société Générale de Surveillance) and provided with the samples, Mg and Al also present in rock samples, however they are invisible in the spectra. This issue was discussed earlier. Unlike fertilizer N-P-K we were provided with the only one sample of each type of N-P and Ca-P fertilizers. Therefore we could not make regular laboratory application study including calibration and verification of the analyzer. However on the basis of the spectral information theoretical analytical precision of measurements were evaluated. In static laboratory conditions accuracy of P, S and Ca measurements is expected to be 0.1 % mass, 0.5 % mass and 0.15 % mass respectively.

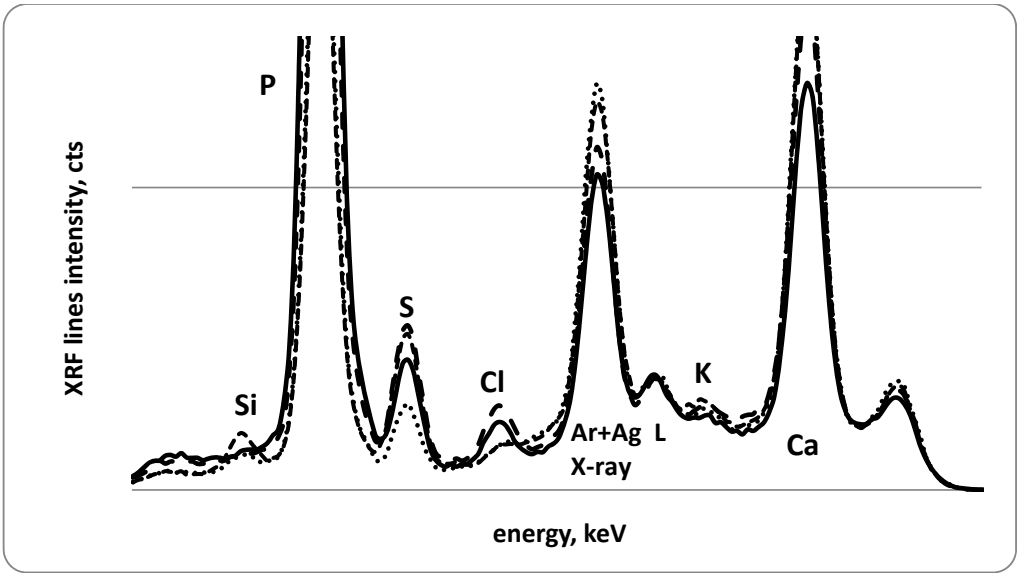

Fig.6. Zoom into the low-intensity lines of the MCP, DCP and rocks spectra. Chemical elements giving rise to the spectral lines are indicated. The lines coding is as on Fig.5.

Spectra on the Figures 5 and 6 confirm the presence of minor amount of Cl and K both in MCP, DCP and rock samples. Their spectral lines are weak due to supposed low concentrations in the measured materials. However the concentrations of these elements can be determine even in 5 minute measurements. Estimated analytical precision for minor components like Cl is on the level of 5 % relative, but for Si and K in rock samples - on the level of 10 % relative due to poor lines intensity.

4. Analysis of uranium as trace element in phosphate rocks and products

Uranium can be found as one of the trace components in phosphate ores and, as a result, in fertilizers, produced from the ores. The world uranium resources in phosphate rock are estimated as $9x10^6$ metric tons of uranium. The average uranium content in phosphate rock, at 50-200 ppm or 0.005-0.020 % mass, is low [6]. In the most situations uranium is left in the produced fertilizer as a radioactive contaminant. Due to literature sources Morocco's uranium resources in phosphate deposits are approximately 6 million tons, which corresponds to twice the world's resources in uranium deposits [6]. Therefore due to health and environmental issues as well as to potential use of phosphate deposits as a source of uranium, application of on-line analyzers for trace uranium measurements is promising [7].

Fig.6 demonstrates spectrum of phosphate Moroccan rock and phosphate fertilizers produced from the rock. Uranium lines are identified in all these materials even in 5 minute measurements.

The limit of detection of the method was quantitatively estimated in line with the procedure 40 CFR part 136 as MDL = (s) * $t_{(n-1,\ 99)}$, where s – standard deviation of replicate analyses (n=10) and $t_{(n-1,\ 99)}$ – the Students' t-value appropriate for 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. Calibration was generated prior to analyzing MDL sample with calibration samples provided by potential Customer. Concentration of uranium in calibration samples were measured in the Customer laboratory by ICP method and covered the range from 30 to 300 ppm. XRF measurements were repeated for 10 replicate solid samples containing 150 ppm of uranium. Samples were not subjected to any treatment besides grinding to the grain size ~ 1 mm and mixing. Thus we sought to keep physical and chemical status of the samples to be as similar to on-line material status as possible.

MDL of uranium estimated by this procedure is 48 ppm. This level of quantification allows analyzer to implement sorting of the raw phosphate rock according to uranium content or monitoring of the uranium level in commercial products (fertilizers) directly on the conveyor belt.

5. Chlorine as a trace element in grounded wet phosphate rock

Apatite group of minerals has the general formula $Ca_5(PO_4)_3X$, where X = F, Cl, OH and/or their mixture. Process of defluorination at high temperatures is used to remove halogens thus upgrading apatite rocks quality. It was proven by laboratory application study that CON-X03M analyzer is capable to measure ppm level of chlorine in wet ground rock in the range from 500 to 2000 ppm. Experimental analytical precision of chlorine measurement is 20 ppm (2.0% relative) in the range 500-2000 ppm, detection limit for 5 minutes measurements is 30 ppm. MDL determination was carried out in the same manner as described in p. 4. Calibration samples were supplied by the potential Customer; they were analyzed in the Customer laboratory by turbidimetric method.

Chlorine content is one of the parameters included in the commercial specifications. Estimated analytical precision and MDL shown in laboratory application study prove that analyzer CON-X03M is capable to measure Cl content in wet ground phosphate rock moving on conveyor belt.

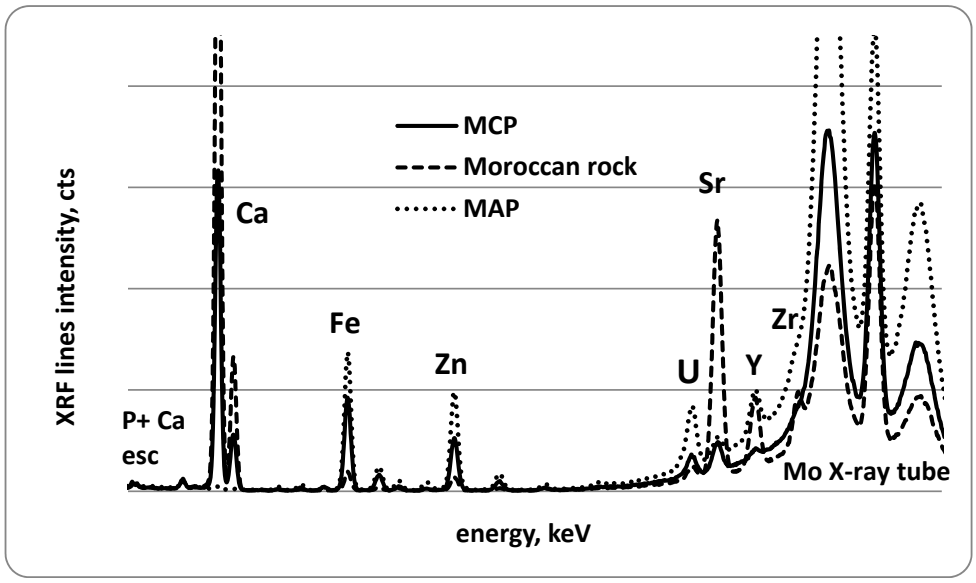

Fig.7. Spectra of Moroccan phosphate ore and products derived from it. Parameters of measurements:
X-ray tube voltage - 39 kV, current – 100 µA, 100 µm thick Mo filter between X-ray tube and sample, measurement time - 600 seconds, distance between sample and detector - 40 mm

6. Conclusions

Laboratory study/calibration, verification test and dynamic simulation of on-line mode showed that XRF on-line analyzer CON-X03M is potentially capable to measure phosphorus, sulphur, potassium and calcium as the main components of different types of phosphorus containing fertilizers directly above the conveyor belt. With the combination of close geometry of the measuring unit and partial air evacuation from the measuring space, intensity of XRF lines of the elements with low atomic numbers is improved. Range of phosphorus content in the fertilizers studied is 1 – 25% mass. Estimated experimental accuracy of P_2O_5 and K_2O determination in N-P-K products is on the level of 2.0 % relative for P and 7.5 % relative for K. Sulphur measurements showed correlation with reference values within 8.5% relative.

On-line measurements of trace amounts of uranium and chlorine in phosphate rocks also can be performed. Estimated MDL for 5 minute measurements on the pilot conveyor is 50 ppm of uranium. MDL of chlorine was determined at 30 ppm in laboratory conditions. The studied concentration ranges are 30 - 300 ppm of uranium and 500 – 2000 ppm of chlorine. At this concentration level estimated experimental accuracy of uranium determination is approximately 30 ppm. Experimental analytical accuracy of chlorine determination obtained in verification lab test is 20 ppm.

Analyzers CON-X series are successfully operating now in different industries and various applications. Potentially application of new conveyor analyzer CON-X03M in industry for measurement of phosphate fertilizers might give the opportunity to estimate quality of commercial goods, discriminate between different grades of fertilizers and adjust corresponding stages of production process. Besides this analyzer is capable to measure minor and trace amounts of associated components of rocks and fertilizers with reasonable accuracy.

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